

# Lithium-Oxygen Batteries: At a Crossroads?

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**Abstract**

In this current opinion, we critically review and discuss some of the most important recent findings in the field of rechargeable lithium-oxygen batteries. We discuss recent discoveries like the evolution of reactive singlet oxygen and the use of organic additives to bypass reactive LiO2 reaction intermediates, and their possible implications on the potential for commercialization of lithium-oxygen batteries. Finally, we perform a critical assessment of lithium-superoxide batteries and the reversibility of lithium-hydroxide batteries.

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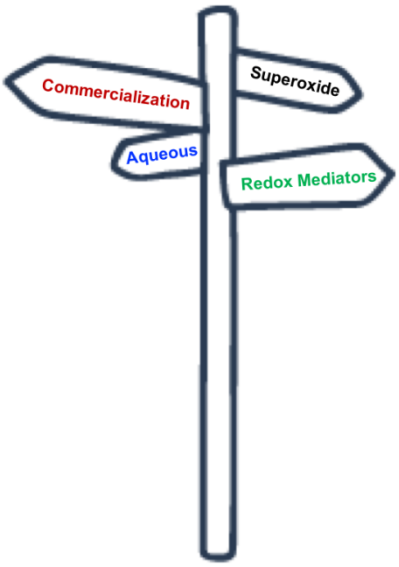
**Highlights**

- Important recent developments in Li-$O_2$ batteries are highlighted
- New additives can bypass the $LiO_2$ intermediate and promote solution phase formation of $Li_2O_2$ in weakly solvating electrolytes
- The role of singlet oxygen and its implications for electrolyte and electrode degradation
- A critical assessment of lithium-superoxide batteries
- Analyzing the reversibility of lithium-hydroxide batteries
- Next-generation Li-$O_2$ electrolytes: Do solid and hybrid electrolytes hold the key?

**Graphical abstract**

Have lithium-oxygen batteries reached a crossroads? Will either of these approaches lead to the commercialization of secondary lithium-oxygen batteries?



# Lithium-Oxygen Batteries: At a Crossroads?

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**Abstract**

In this current opinion, we critically review and discuss some of the most important recent findings in the field of rechargeable lithium-oxygen batteries. We discuss recent discoveries like the evolution of reactive singlet oxygen and the use of organic additives to bypass reactive $LiO_2$ reaction intermediates, and their possible implications on the potential for commercialization of lithium-oxygen batteries. Finally, we perform a critical assessment of lithium-superoxide batteries and the reversibility of lithium-hydroxide batteries.

## Introduction

Secondary lithium-oxygen (Li-$O_2$) batteries remain one of the most hotly pursued and hotly contested future technologies for electrochemical energy storage. Li-$O_2$ batteries offer an alluring theoretical specific energy (~3.500 Wh/kg) – nearly an order of magnitude greater than state-of-the-art in Li-ion batteries (~300 Wh/kg) – yet their practically accessible specific energy remains low.

Two decades after the first report by Abraham and Jiang,[1] and roughly a decade after its scientific light-off,[2,3] more than 1.700 scientific articles have been published on the Li-$O_2$ system, with more than 57.000 citations.[4] This publication activity appears to have peaked in 2015-2016, raising the question whether this 'peak Li-$O_2$' is a consequence of the fundamental mechanisms being fully understood (perhaps with commercialization imminent) or instead a sign of wavering interest from the community?

It is our opinion that neither of these viewpoints is entirely correct. Recent publications clearly document that breakthroughs in understanding and novel approaches to improve performance are still emerging at a rapid pace. At the same time, it is equally clear that near-term commercialization remains elusive. Here, we seek to highlight and review some of the most important recent Li-$O_2$ publications and discuss their potential impact on future research and development of secondary Li-$O_2$ batteries.

## Fundamental Li-$O_2$ mechanisms

In discussing the current progress in the Li-$O_2$ field, a natural distinction is between aqueous and non-aqueous (aprotic) systems, where the latter has received the most attention due to its higher accessible energy density and greater likelihood for reversibility.[5] Nevertheless, a recent publication from Grey *et al.* sparked renewed interest and debate in the aqueous system,[6] as discussed below.

In the aprotic system, two distinctly different mechanisms for oxygen reduction can lead to the formation of the desired $Li_2O_2$ (peroxide) discharge product: (*i.*) a surface-based mechanism, where the $LiO_2$ (superoxide) reaction intermediate binds to the positive electrode surface or to previously deposited $Li_2O_2$, and, (*ii.*) a solution-based mechanism, where the $LiO_2$ intermediate is dissolved in the electrolyte and disproportionates into insoluble $Li_2O_2$ particles/toroids and $O_2$.[7] Which of these mechanisms dominates depends on the relative stability of surface adsorbed $LiO_2$* and $LiO_2$ in solution, where the latter has been

argued to depend on the Gutman acceptor (AN) and donor number (DN) of the electrolyte[8] and the applied ORR potential.[9] For detailed reviews of the different mechanisms in Li-$O_2$, we refer to Aurbach *et al*.[10] and Kang *et al*.[11]

The limitations of the surface-based mechanism are now well understood. For example, the fundamental overpotential for deposition of $Li_2O_2$ is very low (as originally predicted from density functional theory (DFT) calculations[12]), while the high charging potentials observed in early studies employing, e.g., carbonate-based electrolytes are due to parasitic chemistry.[13,14] Independent of electrolyte composition, the insulating nature of the formed $Li_2O_2$ thin-films is the origin of the 'sudden death' during discharge.[15,16,17] At ambient conditions and moderate current densities, the electronic conduction is dominated by tunneling of holes in the valence band of $Li_2O_2$,[18] whereas hole polarons become important at higher temperatures and/or low current densities.[19,20,21,22,23] However, neither mechanism appears capable of providing the electronic conductivity needed to decompose relatively thick $Li_2O_2$ deposits at moderate current densities and with low overpotentials.

**Redox mediators and additives**

In terms of maximizing discharge capacity, the solution-based mechanism easily surpasses the surface-based mechanism. This is possible because the solution mechanism allows the formation of large, micron-sized $Li_2O_2$ particles, typically with toroidal morphologies.[7] However, the electrolytes and impurities that support this mechanism (e.g. water) also increase parasitic side reactions.[24] Also, $Li_2O_2$ particles formed via this mechanism may be located far from the electrode surface, resulting in very slow recharging, or worse, loss of electrical contact (i.e., $Li_2O_2$ stranded on the separator).

The use of redox mediators (RM) could circumvent slow charge transfer between 'distant' $Li_2O_2$ particles and the solid electrode surface. This approach has been investigated intensely since the first report from Bruce *et al*. on the use of the tetrathiafulvalene (TTF) RM.[25] Here, the ($TTF/TTF^+$) redox couple facilitates chemical oxidation of $Li_2O_2$ by acting as a molecular electron-hole transfer agent between $Li_2O_2$ and the electrode surface.[26] A range of different redox mediators have now been investigated, including TEMPO,[27] TDPA,[28] cobaltocene, and ferrocene.[29,8] Nevertheless, this approach has yet to lead to a major breakthrough, in part due to buildup of $Li_2O_2$ and other insulating decomposition products on the electrode surface, which blocks the oxidation of the RM at the electrode. Moreover, RMs often introduce side reactions that may limit performance and can contribute to erroneous conclusions regarding mechanisms. Multiple characterization techniques should therefore be invoked to fully understand their impact.[30]

In an interesting recent publication, Bruce *et al*. showed that using a 2,5-di-*tert*-butyl-1,4-benzoquinone (DBBQ) electrolyte additive can promote solution phase formation of $Li_2O_2$ in low-polarity and weakly solvating electrolytes; thereby apparently dodging the double-edged sword of high capacity but poor stability of the high AN/DN solvents. Since DBBQ also suppresses the surface reduction to $Li_2O_2$, this leads to a capacity increase of up to two orders of magnitude.[31] By utilizing a $LiDBBQO_2$ intermediate, Bruce *et al*. could bypass the $LiO_2$ intermediate in solution, leading to reduced overpotentials for charge and reduced electrolyte degradation resulting from parasitic side reactions (see Fig. 1). Although more work is needed to identify new additive-solvent combinations with improved cyclic performance, the approach shows promise.

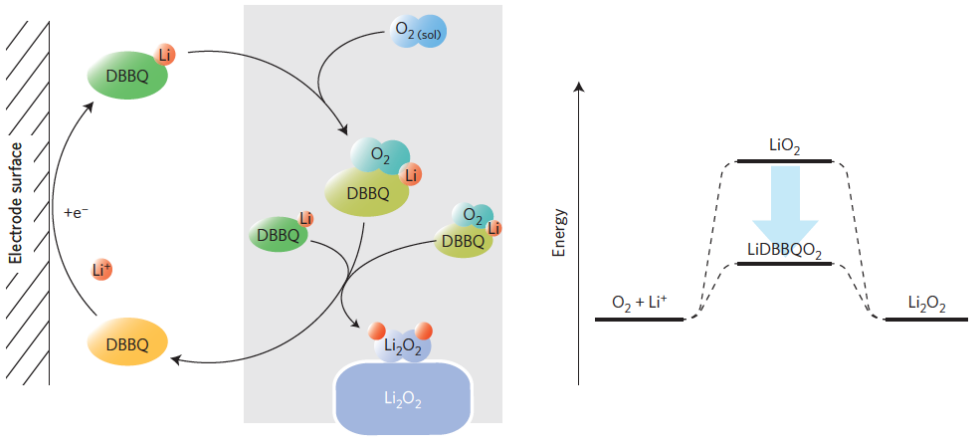


*Fig. 1 Schematics of reactions on discharge (left) and the effect of DBBQ on the potential determining step (right). DBBQ is reduced at the electrode surface, forming LiDBBQ, and then LiDBBQ reacts with $O_2$, producing $Li_2O_2$ and itself being regenerated to DBBQ. The schematic of the free-energy plot is at $E^0$ for $O_2/Li_2O_2$. Reprinted with permission from Ref. 31. Copyright 2017 Nature Publishing Group.*

## Singlet oxygen

The aggressive nature of the strong nucleophiles and bases present in the Li-$O_2$ battery chemistry, *i.e.*, $O_2^-$, $LiO_2$, $Li_{2-x}O_2$ and $Li_2O_2$ species, pose severe challenges for the stability of electrodes, solvents,[32] and salts.[33] It has long been suspected that these reactive species are responsible for the majority of the parasitic reactions that preclude true reversibility, *i.e.* a perfect 1:1 mapping between the amount of $O_2$ consumed during discharge with that released during charge (see Fig. 2).[34,35]

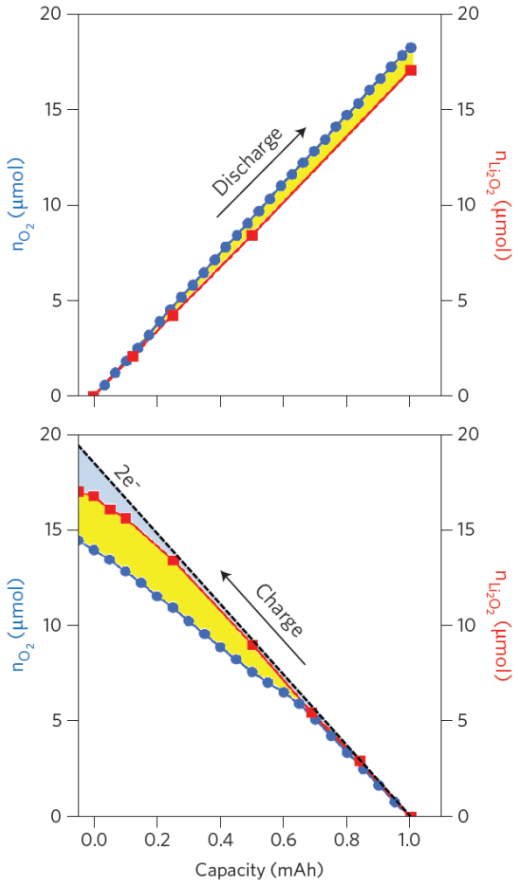


*Fig. 2 Deviation from a truly reversible Li–$O_2$ electrochemistry. Top panel: number of moles of $O_2$ consumed ($nO_2$, blue) and of $Li_2O_2$ formed ($nLi_2O_2$, red) during a 1 mAh Li–$O_2$ discharge. The ideal line for two electrons per $O_2$ consumed is indistinguishable from the blue points. Bottom panel: number of moles of $O_2$ evolved ($nO_2$, blue) and $Li_2O_2$ consumed ($nLi_2O_2$, red) during recharge of*

*the battery above. The ideal line for $2e^-$ consumption reflects the total charging current. The region in yellow for both discharge and charge reflects the parasitic contribution that could arise from singlet oxygen ($^1\Delta_g$). The region in blue on charge is due to parasitic oxidation of species unrelated to $Li_2O_2$ and therefore presumably not related to singlet oxygen formation. Reprinted with permission from Ref. 35. Copyright 2017 Nature Publishing Group.*

A recent discovery by Eichel *et al*., showing that highly reactive singlet oxygen, $^1O_2$, is evolved upon $Li_2O_2$ oxidation at potentials above 3.5 V,[36] could change this perception. Eichel *et al*. demonstrated that singlet oxygen plays a crucial role in the electrolyte degradation and carbon corrosion during charging of the Li–$O_2$ cell. Freunberger *et al*. later documented that singlet oxygen is already produced at the onset of charge and can also be produced via the disproportionation of $LiO_2$ to $Li_2O_2$ and $^1O_2$, and that the amount of $^1O_2$ is enhanced in the presence of water impurities.[37] These interesting findings identify $^1O_2$ as a 'must solve' challenge to achieve reversible cycling by formation/decomposition of $Li_2O_2$. This discovery opens new research directions in the search for new materials and approaches to improve the stability, *e.g*. the use of singlet oxygen traps, as discussed by Luntz and McCloskey.[34]

**Next-generation Li-$O_2$ electrolytes**

Multiple strategies have been proposed to overcome limitations associated with electrolyte stability, including use of alternative electrolyte compositions employing ionic liquids (IL), polymers,[38] IL-polymer composites,[39] and hybrid solid-liquid electrolytes.[40,41] Following the initial promise of ILs,[42,43] subsequent differential electrochemical mass spectrometry (DEMS) studies showed that their stability was ultimately insufficient for practical applications.[44,45] Using a nitrate-based molten salt electrolyte (*i.e.*, an eutectic mixture of $LiNO_3$ and $KNO_3$), Addison *et al.*, however, recently showed very low charge/discharge overpotentials and enhanced rate capability, due to improved stability and moderate solubility of $Li_2O_2$ in this electrolyte. Although promising, the observed capacity loss during cycling was still too high for practical applications.[46]

The use of hybrid solid-liquid electrolytes and all-solid-state electrolytes is also being actively pursued.[47] In an interesting recent study, Luo *et al*. used *in situ* environmental transmission electron microscopy to study the Li-$O_2$ reaction mechanisms in a solid $Li_2O$ electrolyte, yielding valuable insight about the formation and transient disproportionation of metastable $LiO_2$ in solid electrolytes.[48] Further progress in the field of solid-state electrolytes is needed, both in terms of increased solubility of the oxygen reduction species and improved electrolyte conductivity.[49] Substantial improvements are being made in the latter area, *e.g*., through use of garnet ceramic electrolytes like LLZO ($Li_7La_3Zr_2O_{12}$)[50,51,52,53] and nano-structured composite electrolytes,[54] but further work is needed to improve performance during battery charging.

**Lithium-superoxide batteries**

Whereas the related Na-$O_2$ battery chemistry readily forms sodium superoxide ($NaO_2$) as the main discharge product,[55,56] stable superoxide products have remained elusive in the Li-$O_2$ system. Contrary to the conventional behavior of Li-$O_2$ systems, Ammine *et al.* recently reported that cathodes based on reduced graphene oxide (rGO) with added iridium (Ir) nanoparticles yield $LiO_2$ as the main discharge product,[57] sparking massive interest. They observed the formation of large rod-like nanoparticles that were identified as $LiO_2$ based on DEMS, high-energy X-ray diffraction (HE-XRD), and Electron Paramagnetic Resonance (EPR) experiments. The DEMS experiments resulted in an $e^-/O_2$ ratio of 1.00 (1.02) during discharge (charge), which is the main fingerprint of the superoxide formation.[57] The HE-XRD data is compatible with the DFT-predicted $LiO_2$ crystalline marcasite structure[58] (no XRD data of $LiO_2$ has previously been reported, as it is an unstable compound). The EPR signal exhibits a peak at g = 2.1019, consistent with the presence of superoxide ions (peroxide ions are silent in EPR).

Ammine *et al.* suggests a complex route for the formation of the $LiO_2$ nanorods: first, the Ir nanoparticles alloy with Li-ions to give rise to $Ir_3Li$ nanoparticles; second, $LiO_2$ nanorods grow epitaxially on top of the $Ir_3Li$ substrate. The large size of the nanorods is explained through DFT calculations at the Generalized Gradient

Approximation (GGA) level, which showed that $LiO_2$ is a half-metal, allowing the long-range transport of electrons required for the reaction.[57] The metallic nature of $LiO_2$ is, however, still an open question, since other authors have found non-zero bandgaps of 3.6[59]-3.7[60] eV for $LiO_2$ (and 5.3 eV for $NaO_2$[61]), using higher level theory. Similarly, the measured electrical conductivity of other alkali metal superoxides ($KO_2$, $RbO_2$, and $CsO_2$) is poor.[62]

The proposed formation of $Ir_3Li$ nanoparticles is not straightforward from a thermodynamic point of view. The enthalpy of alloying per Ir atom in $Ir_3Li$ has been calculated as -0.4 eV,[63] which is low compared to the experimental enthalpy of formation of rutile $IrO_2$, -2.6 eV per Ir atom.[64] Amorphous $IrO_x$ compounds have also been reported to be very stable.[65] Thus, it seems plausible that oxidation of the Ir nanoparticles could occur at the expense of alloying of Ir and Li.

Once $IrO_2/IrO_x$ nanoparticles are formed, the subsequent formation of $Li_2IrO_3$ nanostructures is conceivable. Indeed, studies by Tarascon *et al.*[66,67] on the electrochemical performance of $\alpha$-$Li_2IrO_3$ and $\beta$-$Li_2IrO_3$ polymorphs provide an alternative interpretation of the results reported by Ammine *et al.* Early studies showed that $\alpha$-$Li_2IrO_3$ displays some peculiarities with respect to related layered materials. First, $\alpha$-$Li_2IrO_3$ is metallic[68] (rutile $IrO_2$ and amorphous $IrO_x$ are also metallic[65]), which would be compatible with the observation of large nanorods in the experiments from Ammine et al. $\alpha$-$Li_2IrO_3$ decomposes into Li, $IrO_2$ and $O_2$ at a relatively low temperature (450 K),[68] which points towards low kinetic barriers for its formation. Furthermore, $\alpha$-$Li_2IrO_3$ can be electrochemically delithiated to $Li_{0.5}IrO_3$.[66,69] Finally, Tarascon *et al.* have shown that the oxidation/reduction of $\alpha$-$Li_2IrO_3$ is very flexible, in the sense that it can happen either at the cations ($Ir^{4+}$ to $Ir^{5+}$) or at the anions ($2{\cdot}O^{2-}$ to peroxo-like $O_2^{3-}$), which are active in EPR experiments.[66] This last property is shared by the $\beta$-$Li_2IrO_3$ polymorphs, which can be electrochemically delithiated to give rise to $IrO_3$.[67] These considerations suggests that a reversible $x{\cdot}(Li^+ + e^- + O_2) + IrO_y \rightarrow Li_xIrO_3$ reaction pathway is also compatible with the DEMS, EPR and HE-XRD measurements (see Fig. 3).

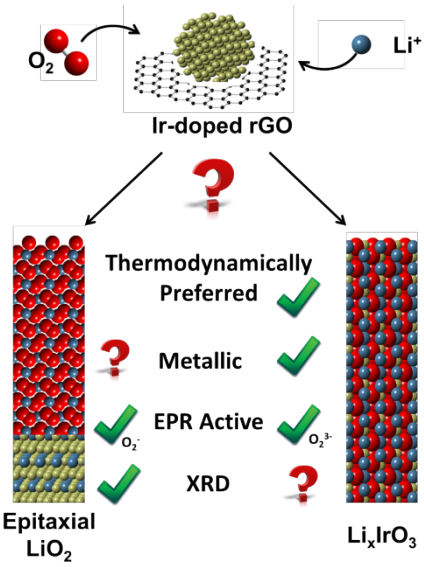


*Fig. 3 Two possible interpretations of the experiments by Ammine at al. using a reduced Graphene oxide (rGo) doped with iridium nanoparticles as a cathode in Li-$O_2$ batteries. On the left, the original interpretation by Ammine et al., in which epitaxial lithium superoxide nanorods on $Ir_3Li$ alloy nanoparticles were hypothesized. On the right, an alternative interpretation based on the formation of lithium iridiate particles. In the middle, the experimental properties which are compatible with each the two interpretations (a question mark means that the compatibility of an experimental property with the corresponding interpretation needs to be investigated).*

### Aqueous lithium-oxygen batteries

In contrast to the well-studied non-aqueous Li-$O_2$ cell, where the discharge product is solid $Li_2O_2$, Liu *et al.* recently demonstrated a system that reversibly cycled LiOH.[6] Other factors being equal, the formation of LiOH as the discharge product is advantageous, as it is more stable than $Li_2O_2$, and may therefore suppress parasitic side reactions. The LiOH cell comprised a macroporous rGO positive electrode, and a DME-based

electrolyte containing water and LiI. In addition to eliminating reactive $Li_2O_2$, the LiOH-based cell exhibited extremely high capacities (>20,000 mAh/$g_{carbon}$) and a discharge-charge voltage hysteresis as low as 0.2 V, corresponding to a round-trip efficiency of 93.2%. The formation of LiOH was claimed to occur via an unusual 4-electron process involving the consumption of water additives in the electrolyte:

$$4Li^+ + 4e^- + O_2 + 2H_2O \rightarrow 4\ LiOH. \qquad (a)$$

This remarkable performance was attributed to several of factors. First, the LiI additions provide redox mediation through the reaction

$$I_3^- + 2e^- \leftrightarrow 3I^-. \qquad (b)$$

Here, $I^-$ is oxidized near the observed charging voltage of 3 V. The resulting $I_3^-$ was proposed to chemically decompose LiOH to water and oxygen gas:

$$4LiOH + 2I_3^- \rightarrow 4Li^+ + 6I^- + 2H_2O + O_2. \qquad (c)$$

Second, the presence of $H_2O$ and LiI induce the growth of relatively large LiOH particles, contributing to the large observed capacity. Finally, the macroporous rGO support also contributes to the formation of large LiOH particles (tens of microns in diameter), while allowing for rapid diffusion of redox active species.

Liu *et al.*'s report of a reversible LiOH battery has sparked vigorous debate. For example, a pair of Technical Comments[70,71] questioned the possibility of chemical decomposition of LiOH by $I_3^-$, via reaction (c), which is uphill in free energy and will thus not occur spontaneously, as suggested. This apparent discrepancy is reflected in the more positive equilibrium voltage of reaction (a), 3.4 V under standard conditions, compared to that of reaction (b), 3.0 V. (This voltage trend is the opposite of what is expected for a viable redox mediator, whose redox potential should slightly more positive than that of reaction (a) being mediated). In their response, Liu *et al.* argued that the non-standard chemical environment of their cell could reduce the voltage of reaction (a) to be closer to the 3.0 V needed for oxidation of $I^-$. Nevertheless, Liu *et al.* cautioned that "the equilibria that occur in the presence of oxygen, water, and iodine are complex…" and "…further mechanistic studies are required to understand the role of these complex equilibria in the redox processes."[72,73]

More recently, Burke *et al*. confirmed the 4-electron process resulting in LiOH formation proposed by Liu *et al*. (reaction (a)) in a cell containing LiI and $H_2O$.[74] However, Burke *et al.* were unable to corroborate the charging mechanism proposed by Liu *et al*. Rather, LiOH was observed to decompose at 3.5 V or higher, which is 0.5 V more positive than in Ref. [6] (see Fig. 4). This higher voltage window was observed to coincide with operation of the $I_3^-/I_2$ couple, and not that of reaction (b). Importantly, LiOH decomposition resulted in the formation of soluble $LiIO_3$, but not $O_2$ evolution, suggesting that the cell is, unfortunately, not truly reversible. Nevertheless, Burke *et al*. concluded that the electrochemistry in cells with different cathode supports, additives, and electrolyte components should exhibit different, and possibly more promising, behavior. Thus, ample opportunities exist to further explore the composition space of this complex system.

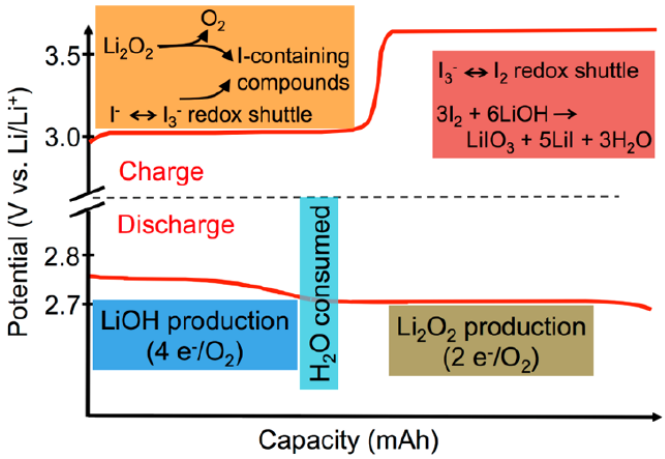


*Fig. 4 Schematic of the mechanisms associated with discharge and charging of a Li/$O_2$ cell with LiI and $H_2O$ additives Reprinted with permission from Ref. 74. Copyright 2016 American Chemical Society.*

**Summary**

Although the fundamental mechanisms in the Li-$O_2$ battery chemistry are becoming increasingly well understood, new insights, interesting concepts, and new challenges continue to emerge. Therefore, we have not yet arrived at the crossroads between commercialization and abandonment.

Several new ideas in the Li-$O_2$ system have recently emerged, warranting additional research, *e.g.* the use additives such as BDDQ, which can help bypass the $LiO_2$ intermediate and thereby enable more stable electrolytes like ethers with low DN and combine to yield higher rates, capacity and cycle-life. It is, however, imperative that when new redox mediators or additives are introduced, careful quantitative analysis and characterization is performed using complementary techniques, as the true origin of a new mechanism may well be hidden under the surface.

An improved understanding of the complexity of the decomposition reactions during charging is still needed. This includes clarifying the exact conditions for generation and suppression of singlet oxygen, and the identification of suitable quenching agents with a sufficiently high electrochemical stability window. These questions appear far more vital than continued investigations of ORR/OER catalysts, which in our opinion have been overemphasized.

Finally, solid or hybrid electrolytes could hold the key to the development of more stable electrolytes strategies, but research for these materials is in its infancy, with many fundamental questions still to be answered.

**Acknowledgements**

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